

PATENT SPECIFICATION

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(54) MANUFACTURE OF FLEXIBLE THERMOPLASTICS FOAMS

(71) We, BASF AKTIENGESELLSCHAFT, a German Joint Stock Company of 6700 Ludwigshafen, Federal Republic of Germany, do hereby declare the invention, for which we pray that a Patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following Statement:—

The present invention relates to a process for the manufacture of a flexible foam of a thermoplastic olefin polymer by heating a mixture of an ethylene polymer and/or a chlorinated polyethylene of certain types, an organic peroxide as crosslinking agent and an expanding agent in a confined gas-tight zone in which there is initially virtually no gas space, to soften the polymer and decompose the expanding and crosslinking agents, whereby a pressure is generated within the zone, releasing the pressure and allowing the expandable mixture to foam.

German Published Application 1,919,748 describes a process for the manufacture of foams of thermoplastic ethylene polymers. In this process, a thermoplastic ethylene polymer is mixed with an organic peroxide as crosslinking agent and an expanding agent and the resulting expandable mixture is heated in a gas-tight mold, in which there is initially virtually no gas space, to temperatures at which the ethylene polymer has softened and the expanding and crosslinking agents have decomposed, thereby generating a pressure in the mold, whereupon the volume of the mold is enlarged so as to release the pressure on the molten expandable mixture which then expands to form a foam, and the foam is then cooled. Prior art foams formed in this way do not have optimum properties in a number of applications.

The present invention seeks to provide a process for the manufacture of flexible foams having a finer cellular structure, better mechanical properties and lower thermal

conductivity than prior art foamed plastics.

According to the present invention there is provided a process for the manufacture of a flexible foam of a thermoplastic olefin polymer which comprises heating an expandable mixture comprising a thermoplastic ethylene polymer having an X-ray crystallinity at 25°C or more than 20% by weight and/or a chlorinated polyethylene having a chlorine content of 10 to 45% by weight, an organic peroxide as crosslinking agent and an expanding agent in a confined gas-tight zone in which there is initially virtually no gas space to an elevated temperature at which the polymer has softened and the expanding and crosslinking agents have decomposed, whereby an excess pressure is generated in the zone, cooling the outer surface of the expandable mixture to such an extent that the difference between the temperature of the outer surface of the expandable mixture and the maximum temperature within the expandable mixture is from 10° to 100°C, and thereafter releasing the excess pressure on the expandable mixture and allowing it to foam.

The process of the invention surprisingly is able to produce foamed plastics having a particularly fine cellular structure and an extremely high resistance to water vapor diffusion therethrough. It was not foreseeable that the mechanical properties of these foams, e.g. their elongation at break and their tensile strength as measured according to DIN 53,571, would be improved over foams made by prior art processes.

The ethylene polymers are crystalline polymers having an X-ray crystallinity at 25°C of more than 20% by weight. Both homopolymers and copolymers of ethylene are suitable for the process. For example, copolymers of ethylene with one or more other olefins such as propylene and n-butene may be used. Also suitable are copolymers of ethylene which contain up to

40% by weight of polymerized units of one or more acrylates or methacrylates or esters of other ethylenically unsaturated carboxylic acids. Copolymers of ethylene with one or more vinyl carboxylates and copolymers obtained by copolymerization of ethylene with t-butyl acrylate or methacrylate or isopropyl acrylate or methacrylate are also suitable. The conditions of manufacture of the polymers may be selected so that a portion of the copolymerized acrylate forms copolymerized free acid groups with elimination of isobutylene or propylene. These ethylene copolymers then contain from 0.1 to 7% molar of copolymerized carboxylic acid groups. The comonomer content of said ethylene polymers is generally in the range of 5 to 30% by weight. Blends of said polymers may be used, for example blends of 80% of high-pressure polyethylene and 20% of an ethylene/vinyl acetate copolymer, by weight. The melt index of the ethylene polymer is from 0.1 to 22 g/10 min. (as measured according to ASTM D 1238-65 T).

Also suitable for the process is chlorinated polyethylene containing from 10 to 45% by weight of chlorine, which may be used in admixture with post-chlorinated polyvinyl chloride. We prefer to use polyethylene, ethylene/propylene copolymers and chlorinated polyethylene.

An organic peroxide is used as crosslinking agent. As is usual, the peroxide selected should cause little or no crosslinking of the polymers at the temperature to be used when mixing the polymer, expanding agent and crosslinking agent. Thus particularly suitable products are those which cause crosslinking only at relatively high temperatures, preferably at temperatures of from 10° to 80°C above the softening range of the polymer, e.g. 1,3-bis-(t-butylperoxyisopropyl)benzene, dicumyl peroxide and t-butylcumyl peroxide. In general, the crosslinking agent is used in an amount of from 0.05 to 2.5% and preferably from 0.1 to 1.5% by weight of the weight of polymer.

Particularly successful expanding agents are chemical foaming agents. These are mainly solid compounds which decompose at elevated temperatures to form gaseous decomposition products. Advantageously, the expanding agents selected decompose at from 15° to 150°C above the softening range of the polymer. The decomposition temperature of the expanding agent is conveniently from 5° to 70°C above the decomposition temperature of the crosslinking agent.

Examples of expanding agents which can be used in the process of the invention are azodicarbonamide, p-carbomethoxy-N-nitroso-N-methyl benzamide, azoisobutyronitrile, N,N'-dinitrosopentamethylene tetramine, N-nitroso-N-alkyl amides of aromatic

dicarboxylic acids, trans-N,N'-dinitroso-N,N'-dimethylhexahydro terephthalamide, N,N'-dinitroso-N,N'-dimethyl terephthalamide and diphenylsulfone-3,3'-disulfonylhydrazide.

The expanding agents are suitably contained in the polymer mixture in amounts of from 8 to 20% and advantageously from 11 to 13% by weight of the weight of polymer.

During manufacture of the expandable mixture of polymer, expanding agent and crosslinking agent it is possible to incorporate a variety of additives such as dyes, fillers, lubricants, pigments, flame-proofers, fibers (glass fibers), inert fillers and catalysts for accelerating the decomposition of the expanding agent. Such decomposition catalysts, for example basic lead sulfate, lead stearate or epoxidized soy bean oil, are used particularly if chlorinated polymers are employed, since they stabilize the chlorinated polymers used.

The mixtures of polymer, crosslinking agent, expanding agent and any other additives are suitably homogenized in mixing units of the type commonly used in the plastics industry. The mixtures to be processed into foams may for example be in the form of crepes having a thickness of from 1 to 10 mm as obtained by removing the mixture from calenders or mixing rollers. However, the starting mixtures may also be in the form of granules, ropes, irregularly shaped particles or compressed boards. As is usual, however, the mixtures will be made in such a manner that the polymers are sufficiently softened to render them plastic and thus make it possible to achieve homogeneous mixing. As is usual, the mixing operation is desirably carried out at as low a temperature as possible, little or no decomposition of the crosslinking agent will occur during mixing. Since the decomposition temperature of the expanding agents as used in the process of the invention is usually higher than that of the peroxide crosslinking agent, gas generation from the expanding agent should not occur during mixing. A particularly economical method of making the mixtures is to use extruders for this purpose, since the mixture may then be readily obtained in the form of granules. The ingredients are generally mixed at temperatures of from 110° to 125°C.

In order to manufacture foams showing no voids, it is essential to heat the expandable mixture in a confined gas-tight zone and to fill the zone with the expandable mixture to such an extent that the zone, when close, initially exhibits virtually no gas space. For this purpose the zone is suitably filled with the expandable mixture of polymer, expanding agent and crosslinking

agent to an initial extent of from 96 to 100% by volume. This ensures that the gas generated from the expanding agent is almost completely dissolved in the melt.

- 5 Preferably, the mixture of polymer, expanding agent and crosslinking agent is enclosed in a gas-tight zone formed by placing an at least 3 mm thick base plate having a central recess on the lower portion of a
10 press provided with heating means and covering said base plate with a metal sheet having a thickness of at least 1 mm. If the plunger of a press is then lowered against the metal sheet under high pressure, the mix-
15 ture of polymer, expanding agent and crosslinking agent is enclosed in the recess forming a gas-tight cavity. It is convenient to use base plates in which the recess is square or nearly square. The recess in the
20 base-plate may extend over the entire thickness of the base-plate, for example when, say, a square piece is cut out of a base plate having a thickness of at least 3 mm. In this case it is necessary to place an
25 underplate on the lower part of the press and then place the base plate containing a hole on said underplate.

The process of the invention may also be carried out using the equipment described in

- 30 U.K. Patent Specification 1,297,197.
The mixture of polymer, expanding agent and crosslinking agent in the press, after it has been enclosed in the recess forming a gas-tight cavity, is heated to a temperature
35 at which the expanding agent and the crosslinking agent have both decomposed. The temperature necessary depends on the type of polymer and on the decomposition temperatures of the expanding and crosslinking
40 agents. It is generally from 160° to 240°C and preferably from 170° to 190°C.

- The essential characterizing feature of the present invention is that the resulting expandable mixture is held
45 under pressure and its outer surface cooled to such an extent that a temperature difference of from 10° to 100°C exists between the maximum temperature in the interior of the expandable melt and the temperature of the outer surface. When
50 this temperature difference has been established, the expandable mixture is allowed to expand by releasing the pressure and enlarging the space available for expansion. The
55 said temperature difference within the expandable mixture may conveniently be established by cooling the heating plates present on the press. The optimum temperature difference is dependent on the polymer.
60 The conditions may differ for different presses, different heating conditions and different dimensions of the base plate. The optimum temperature difference within the expandable mixture must in most cases be
65 determined experimentally. This cooling of

the pressurized expandable mixture prevents or substantially prevents tearing the molten foam at the outer zones during the sudden expansion.

The expandable mixture foams as soon 70 as the plunger of the press is raised. It then fills all available space. Whereas in the process described in German Published Application 1,919,748 the melt preferentially expands upwardly, the expandable melt 75 tends to expand laterally in the present process. The shaped articles thus formed show greater side-to-side dimensions than those produced in the prior art process. A frame may be placed on the base 80 plate to restrict the lateral expansion of the foam. In general, after expansion has taken place, the foam has a volume which is from 3 to 35 times and preferably from 10 to 20 times the volume of the original expand- 85 able mixture. The expandable mixture normally foams over a period of from about 1 to 10 seconds. The density of the shaped foams produced by the process of the invention is usually from 25 to 100 and pre- 90 ferably from 30 to 50 g/l. The foams produced in the present process shown greater compactness at their surfaces than in their interior and this fact lends them a high degree of abrasion resistance, greater than 95 that obtained in prior art foamed articles. The foams also show a higher degree of energy absorption under impact than similar prior art foams.

The foams produced in the process of the invention have high dynamic damping values and high compression hardness and are easy to deep-draw and weld. They may be bonded, printed, embossed and laminated with metals. They are used, for example, in the automobile industry for lining trunks, 100 roofs and sides of vehicles and for sealing purposes. The foams produced in the invention are also used in the building industry for back-filling joints and as heat-insulating 105 layers, as sealing elements and for covering facades in the form of metal-foam-metal sandwich assemblies. The foams are also used for packaging purposes.

In the following Examples the parts are 115 by weight.

EXAMPLE 1

A steel plate measuring 700 × 700 × 2 mm is placed in a high-pressure press in which the plunger covers an area of 750 × 120 750 mm. On the said steel plate there is placed a base plate measuring 700 × 700 × 15 mm and containing a hole in the center, the dimensions of which are 250 × 250 × 15 mm. A mixture of polymer, 125 expanding agent and crosslinking agent is then placed in the hole and a steel plate measuring 700 × 700 × 2 mm is finally placed over the hole to form a cover-plate, thereby rendering the hole gastight. 130

6,000 parts of polyethylene having a density of 0.918 g/cm³, a melt index of 1.2, an X-ray crystallinity at 25°C of more than 20% by weight, a crystallite melting point of 105°C, a softening range of 110 to 115°C and a modulus of elasticity (DIN 53,547) of 1,500 kg/cm², 24 parts of 1,3-bis-(t-butylperoxyisopropyl)benzene (decomposition temperature 150°C), 60 parts of zinc stearate 100 parts of talc and 660 parts of azodicarbonamide (decomposition temperature below 180°C in the presence of zinc stearate and talc) are mixed together at 120°C in a roller mill. The mixture is obtained in the 15 form of crepes having a thickness of 4 mm. The crepes are stacked in the hole of the base-plate of the mold described above so that the hole has no free gas space when the mold is closed. The press is then closed under a pressure great enough to ensure that the mold containing the expandable mix remains gas-tight.

The mixture is then heated for 12 minutes at 180°C. Cooling water is then 25 passed through the heating plates on the press for 20 seconds until the temperature of said heating plates has dropped to 120°C. After a further 3 minutes, the applied pressure is released over a period of from 1 to 30 3 seconds. The expandable melt formed in the hole of the base-plate expands to a foam measuring 600 × 600 × 40 mm. Immediately after the formation of the foam, the temperature in its outer zones is 35 120°C, whereas the temperature at the center of the foam is 145°C. The time taken for heating, cooling and removal of the molding in the form of a foamed panel is about 60 minutes. The foam has a density of 38 g/l, a tensile strength (DIN 53,571) of 4.7 kg/cm², an elongation at break (DIN 53,571) of 167% and a coefficient of thermal conductivity (DIN 52,612) of 0.030 kcal/mhr°C at 0°C.

45 COMPARATIVE EXAMPLE

The mixture described in Example 1 is heated for 12 minutes at a temperature of 180°C in an apparatus as described in Example 1 of German Published Application 1,919,748, and foaming is carried out at a temperature of 180°C without previous cooling. To this end, the applied pressure is released over a period of from 1 to 3 seconds. The mold is then cooled to 55 about 60°C. There is obtained a foam having a thickness of 100 m and a density of 44 g/l. The tensile strength (DIN 53,571) is 1.7 kg/cm², the elongation (DIN 53,571) is 125% and the coefficient of thermal conductivity (DIN 52,612) is 0.0375 kcal/mhr°C at 0°C.

EXAMPLE 2

Using a conventional kneader and an extruder and granulating equipment as 65 normally used in industry, 60 kg of a mix

containing a number of ingredients is homogenized at a temperature of 125°C and granulated. The resulting granules have a diameter of from 325 mm. The mix used for this process consists of the following ingredients: 1,000 parts of a copolymer of 81% by weight of ethylene and 19% by weight of n-butyl acrylate (melt index 1 to 2.5 g/10 min., X-ray crystallinity at 25°C greater than 20% by weight, softening point about 92°C and modulus of elasticity 340 kg/cm²), 6 parts of dicumyl peroxide (decomposition temperature 160°C), 110 parts of azodicarbonamide (decomposition temperature in the presence of zinc stearate below 170°C), 2 parts of a thermostabilizer and 10 parts of zinc stearate.

The granules are fed to the apparatus described in Example 1 to fill the cavity 85 in the base plate so that this again exhibits no gas space when the press is closed. After closure of the press, the mix is heated for 15 minutes at a temperature of 170°C in the gastight mold, whereupon 90 cooling water is passed through the heating plates for 30 seconds until the temperature in the outer zones of expandable melt is 100°C (this temperature being the same as that of the heating plates). The temperature 95 of the outer zones of the expandable melt is held at 100°C for 3 minutes and the applied pressure is then rapidly removed. There is obtained a foam measuring 630 × 630 × 41 mm, its temperature at the 100 center being 130°C immediately after formation. This foam has a density of 36 g/l and a dense skin showing very fine pores. The foam has very fine cells compared with prior art foams. It may be used as interior 105 trim for automobiles.

EXAMPLE 3

Crepes having a thickness of 4 mm are formed in a roller mill at a temperature of 110°C from the following components: 110 2,000 parts of chlorinated polyethylene having a chlorine content of 25% by weight, a softening range of 90 to 95°C and a modulus of elasticity (DIN 53,457) of 520 kg/cm², 6 parts of 1,3-bis-(t-butylperoxyisopropyl)benzene, 220 parts of azodicarbonamide, 20 parts of zinc stearate, 20 parts of lead stearate, 60 parts of basic lead sulfate and 1 part of cadmium sulfide. The crepes are placed in an apparatus as described in Example 1 in such a manner that 120 the hole in the base plate is completely filled. The crepes are heated in the sealed mold for 16 minutes at a temperature of 180°C at which temperature the expanding 125 and crosslinking agents have decomposed. Water is then passed through the heating plates until the outer zones of the expandable melt have a temperature of 90°C. This temperature is maintained for 3 minutes 130

and the press is then opened quickly. There is obtained a foam measuring $700 \times 700 \times 45$ mm. Immediately after formation of the foam, its outer zones have a temperature of 90°C and its interior has a temperature of 130°C . The foam has a density of 52 g/l , has very fine cells and is flexible and suitable, for example, for use as inserts in life jackets.

10 EXAMPLE 4

A mixture of 3,000 parts of copolymer of ethylene and propylene in a molar ratio of 1:1 (density 0.87 g/cm^3 , X-ray crystallinity at 25°C greater than 20% by weight, softening point about 60°C , molecular weight about 95,000), 375 parts of azodicarbonamide, 30 parts of zinc stearate, 9 parts of 1,3-bis-(t-butyl peroxyisopropyl) benzene and 15 parts of triallyl cyanurate is mixed in a twin-roller mill at a temperature of 80°C to form crepes having a thickness of 5 mm. The crepes are placed in the hole of the apparatus described in Example 1 so that they completely fill the cavity of the mold when pressing is commenced. The mixture is then heated for 15 minutes at a temperature of 175°C , at which temperature the expanding and crosslinking agents have decomposed, whereupon the heating plates are cooled until the temperature of the outer zones of the expandable mixture has fallen to 70°C . The applied pressure is then released immediately. There is produced a highly flexible foam containing fine cells and measuring $650 \times 650 \times 40$ mm, its density being 49 g/l . Immediately after foaming, the skin of the foam has a temperature of 70°C , whilst its temperature at the center is 125°C . These foams may be used for all types of upholstery.

WHAT WE CLAIM IS:—

1. A process for the manufacture of a flexible foam of a thermoplastic olefin polymer which comprises heating an expandable mixture comprising a thermoplastic ethylene polymer having an X-ray crystallinity at 25°C of more than 20% by weight and/or a chlorinated polyethylene having a chlorine content of 10 to 45% by

weight, an organic peroxide as crosslinking agent and an expanding agent in a confined gas-tight zone in which there is initially virtually no gas space to an elevated temperature at which the polymer has softened and the expanding and crosslinking agents have decomposed, whereby an excess pressure is generated in the zone, cooling the outer surface of the expandable mixture to such an extent that the difference between the temperature of the outer surface of the expandable mixture and the maximum temperature within the expandable mixture is from 10 to 100°C , and thereafter releasing the excess pressure on the expandable mixture and allowing it to foam.

2. A process as claimed in claim 1 wherein the polymer used is polyethylene or an ethylene/propylene copolymer.

3. A process as claimed in claim 1 or 2 wherein the crosslinking agent is 1,3-bis-(t-butylperoxyisopropyl)benzene, dicumyl peroxide or t-butylcumyl peroxide and is used in an amount of from 0.05 to 2.5% by weight based on polymer.

4. A process as claimed in any of claims 1 to 3 wherein the expanding agent decomposes at a decomposition temperature which is from 5 to 70°C above the decomposition temperature of the crosslinking agent and is present in an amount of from 8 to 20% by weight based on the polymer.

5. A process as claimed in any of claims 1 to 4 wherein the expandable mixture is heated to a temperature of from 170 to 190°C .

6. A process for the manufacture of a flexible foam of a thermoplastic olefin polymer carried out substantially as described in any of the foregoing Examples 1-4.

7. A flexible foam of a thermoplastic olefin polymer when manufactured by a process as claimed in any of claims 1 to 6.

J. Y. & G. W. JOHNSON,
Furnival House,
14-18 High Holborn,
London WC1V 6DE.
Chartered Patent Agents,
Agents for the Applicants.